Source and age of dissolved and gaseous carbon in a peatland-riparian-stream continuum: a dual isotope (^{14}C and $\delta^{13}C$) analysis

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Abstract

Radiocarbon isotopes are increasingly being used to investigate the age and source of carbon released from peatlands. Here we use combined ^{14}C and $\delta^{13}C$ measurements to determine the isotopic composition of soil and soil decomposition products (dissolved organic carbon (DOC), CO_2 and CH_4) in a peatland-riparian-stream transect, to establish the isotopic signature and potential connectivity between carbon pools. Sampling was conducted during two time periods in 2012 to investigate processes under different temperature, hydrological and flux conditions. Isotopic differences existed in the peatland and riparian zone soil organic matter as a result of the riparian depositional formation. The peatland had a mean radiocarbon age of 551 ± 133 years BP, with age increasing with depth, and $\delta^{13}C$ values consistent with C3 plant material as the primary source. In contrast the riparian zone had a much older radiocarbon age of 1055 ± 107 years BP and showed no age/depth relationship; $\delta^{13}C$ in the riparian zone was also consistent with C3 plant material. With the exception of DOC in September, soil decomposition products were predominately >100 %modern with ^{14}C values consistent with derivation from organic matter fixed in the previous 5 years. Emissions of CO_2 and CH_4 from the soil surface were also modern. In contrast, CO_2 and CH_4 evaded from the stream surface was older (CH_4: 310-537 years BP, CO_2: 36 years BP to modern) and contained a more complex mix of sources combining soil organic matter and geogenic carbon. The results suggest considerable vertical transport of modern carbon to depth within the soil profile. The importance of modern recently fixed carbon and the differences between riparian and stream

isotopic signatures suggests that the peatland (not the riparian zone) is the most important source of carbon to stream water.

Keywords: Aquatic export, Carbon, Peatland, Riparian zone, Radiocarbon, ^{13}C

1 Introduction

Peatlands are an important global carbon store, containing around one third of total soil carbon, despite only covering 2-3 % of the land surface (Gorham, 1991; Turunen et al. 2002). Future climatic and anthropogenic changes have the potential to alter the ability of peatlands to store carbon by modifying both land-atmosphere and aquatic export pathways. It is therefore important to understand the current sources, ages and proportions of each carbon species in order to predict the impacts of future change scenarios (Billett et al. 2010). The net ecosystem carbon balance (NECB) of a peatland is a function of the net ecosystem exchange (NEE) of CO_2 between the ground surface and the atmosphere, the emission of CH_4 and downstream export (Chapin et al. 2006). Downstream carbon export consists of particulate and dissolved organic and inorganic carbon (POC, DOC, DIC), and dissolved CO_2 and CH_4 plus vertical evasion of CO_2 and CH_4 from the water surface to the atmosphere (Billett and Harvey 2013; Limpens et al. 2008). To date, much of the focus has been on land-atmosphere exchange, but due to the importance of headwater streams in carbon release at both catchment and regional scales (Cole et al. 2007), the aquatic pathway has now been recognised as an important component of the NECB accounting for 31-51 % of uptake via NEE (Dinsmore et al. 2010; Nilsson et al. 2008; Roulet et al. 2007). For example, at Auchencorth Moss, a temperate peatland in SE Scotland, the mean annual aquatic carbon export over the period 2007-2011 was 35.6 g C m^{-2} yr^{-1}, dominated by downstream losses of DOC (19.3 g C m^{-2} yr^{-1}) and CO_2 evasion (10.0 g C m^{-2} yr^{-1}) (Dinsmore et al. 2013).

The concentration, speciation and isotopic composition of carbon in stream waters is the result of terrestrial and aquatic carbon inputs, interactions with geological and atmospheric sources, and processing and transformations within the stream channel (Striegl et al. 2007). In many northern hemisphere peatland headwaters in-stream aquatic carbon production is limited by low temperature, low pH and short stream residence times (Dawson et al. 2001) resulting in stream water organic carbon being predominately of terrestrial origin. The terrestrial soil carbon pool, consisting of soil organic matter, DOC, CO_2 and CH_4, is heterogeneous, particularly with depth, due to differences in production and transport mechanisms. The composition of the terrestrial carbon pool and

connectivity between the pools and the stream channel are the dominant controls on the concentration and speciation of carbon within headwater streams (Fiebig et al. 1990; Vidon et al. 2010; Dinsmore et al. 2008). In stable peatlands the carbon cycle is likely to be dominated by relatively modern carbon with older carbon stored at depth (Moore et al. 2013). The isotopic signature of carbon released from peatlands is therefore an indicator of the dominant carbon cycling processes and peatland stability (Moore et al. 2013).

Recent methodological advances have overcome many of the limitations of isotopic methods; principally the relatively large sample volumes required for ^{14}C analysis and the low carbon concentrations and flux rates found in natural systems. Methods now exist for analysis of both ^{14}C and $\delta^{13}C$ in soil, soil CO_2, CH_4 and DOC (Garnett et al. 2011), soil emitted CO_2 and CH_4 (Garnett et al. 2012b), stream water DOC and CO_2 and CH_4 evaded from the stream surface (Garnett et al. 2012c).

Soil ^{14}C age has been found to increase with depth down the soil profile, due to peat depositional processes, from modern in near-surface layers to several thousands of years BP at depth (Charman et al. 1999; Clymo and Bryant 2008; Palmer et al. 2001). The decomposition of these soils under either oxic or anoxic conditions, depending on water table conditions, produces DOC, CO_2, and CH_4. Again these generally show an increasing age-depth profile from modern to 4330 year B.P for CO_2 and modern to 3960 years BP for CH_4; both gases being generally ^{14}C enriched relative to the surrounding peat (Charman et al. 1999; Chasar et al. 2000; Clymo and Bryant 2008; Garnett et al. 2011). Similarities in the age profiles of the different carbon species are considered a sign of derivation from a similar source, namely soil organic matter (Clymo and Bryant 2008).

To our knowledge, only four previous studies have analysed the ^{14}C content of CH_4 emitted from the peatland surface. Three give values in the range of 111 to 123 %modern, although these are limited to North America (Chanton et al. 1995; Quay et al. 1991; Wahlen et al. 1989). Combined with $\delta^{13}C$ values between -56 and -73.5 ‰ they indicate a significant component of recently fixed, bacterially produced CH_4. Recent work by Garnett et al. (2012b) found ^{14}C depleted CH_4 from a Scottish peatland in the range 84.69 to 97.89 %modern (1399 to 195 years BP), which may indicate a component of older, deep peat derived CH_4. Although ^{14}C values >100 %modern indicate that there is a significant component of carbon fixed since ~AD 1955, it does not preclude a component of carbon fixed pre-bomb (before ~AD 1955). Surface respiration is therefore likely to be a complex mix of multiple end members including soil and plant respiration, plant-mediated transport of older CO_2 and CH_4 from deeper in the peat and ^{13}C enriched sources, such as the weathering of carbonate material within the soil (Garnett and Hardie 2009; Hardie et al. 2009).

Gaseous carbon dissolved in stream water was found to be <100 %modern in the range 707-1210 years BP in the Black Burn draining Auchencorth Moss (the peatland studied here), with a strong correlation between age and discharge with younger carbon released during periods of higher flow (Garnett et al. 2012a). Peatland headwater streams have consistently been found to be supersaturated in CO_2 and CH_4 relative to the atmosphere (Hope et al. 2001; Kling et al. 1991). This, combined with the turbulent nature of these streams, results in significant evasion from the stream surface (Billett and Harvey 2013; Billett and Moore 2008; Jones and Mulholland 1998). Evaded CO_2 from Auchencorth Moss was found in the range ~850-1450 years BP (Billett et al. 2006) and from other catchments from modern to 1450 years BP (Billett et al. 2007) with the source of this evaded carbon representing a mix of soil derived, geogenic and atmospheric carbon. To date, the only study to measure the ^{14}C age of CH_4 evaded from peatland streams is Garnett et al. (2012c). Evaded CH_4 (1617-1987 years BP) was found to be considerably older than CO_2 (303-521 years BP); suggesting CH_4 was derived from deeper horizons within the peat profile compared to CO_2.

DOC has been found in the soil carbon pool ranging from modern to 6970 years BP (Chasar et al. 2000; Clymo and Bryant 2008; Chanton et al. 2008). Despite this, DOC in peatland headwater streams has been shown to be primarily modern and derived principally from the decomposition of recently fixed organic matter (Billett et al. 2007; Mayorga et al. 2005; Schiff et al. 1997). However, some degraded systems release old carbon into the stream channel in both gaseous and dissolved forms (Frey and Smith, 2005; Guo and Macdonald 2006; Moore et al. 2013).

Peatland vegetation, which uses the C3 photosynthetic pathway, results in soil and DOC from soil decomposition having $\delta^{13}C$ values in the range ~ -25 to -30 ‰, although Clymo and Bryant (2008) found a narrower range between -26.2 ‰ at the surface to -27.3‰ at 7 m depth. The anaerobic decay of soil organic matter produces ^{13}C depleted CH_4 and ^{13}C enriched CO_2 relative to the source material (Hornibrook et al. 2000; Waldron et al. 1999). Garnett et al. (2011) found $\delta^{13}C$ values of CO_2 increased with depth from -12.4 ‰ at 25 cm depth to +8.3 ‰ at 4 m. By contrast the CH_4 $\delta^{13}C$ values were in the range -58.4 ‰ to -70.6 ‰. The $\delta^{13}C$ values when combined with ^{14}C give a clearer understanding of the decomposition processes occurring within peatlands while providing a means of identifying the sources of exported carbon.

Most of the studies above, with the exception of Palmer et al. (2001), have focused only on the central areas of peatland bodies, where peat deposits are thickest and most stable. However, it is changes in riparian zones, at the interface between the terrestrial and aquatic systems, which are likely to have the greatest impact on stream

water isotopic composition. Riparian zones, as the final area of soil that water passes through before becoming surface runoff (Burt, 2005) have a key role in controlling the hydrological response of the catchment (McGlynn and McDonnell, 2003) and the movement of water and solutes across the terrestrial-aquatic interface (Fiebig et al. 1990; Lyon et al. 2011). Stream-riparian linkages are reciprocal with streams causing erosion, flooding and sediment deposition on riparian zones, especially during periods of high flow (Luke et al. 2007; Naiman and Décamps 1997). These characteristics, combined with the redox conditions, result in the riparian zone being a dynamic and complex environment capable of transforming biochemical cycles, including carbon (Ranalli and Macalady 2010; Vidon et al. 2010). In agricultural systems, riparian zones have been found to be hotspots for denitrification, acting as a significant buffer for nitrate transport between the terrestrial and aquatic systems (Naiman and Décamps 1997). Despite the importance of riparian zones, their role in the production, transport and transformation of carbon between the terrestrial and aquatic systems in peatlands has received little attention.

To our knowledge this is the first time isotope techniques have been used to examine the role that the riparian zone in peatlands plays in determining stream water composition. The study combines ^{14}C and $\delta^{13}C$ analysis of the terrestrial peatland and riparian carbon pools and soil-atmosphere emissions, with the aquatic carbon export and emission pathways to test the following hypotheses:

1. The isotopic composition of soil organic matter, DOC, CO_2 and CH_4 are distinct in riparian and peat soils, related to differences in the soil depositional processes and the cycling of carbon.

2. CO_2, CH_4 and DOC within stream water have a similar isotopic signature to the riparian zone, indicating the importance of the riparian zone as a source for stream export.

3. Soil emissions and stream export are composed predominately of modern carbon, indicating that overall the peatland is stable and processing recently fixed carbon.

2 Methods

2.1 Site Description

Auchencorth Moss is a 3.4 km^2 low lying (250-300 m above sea level), ombrotrophic peatland catchment situated 17 km south of Edinburgh, UK (55°47’34N; 3°14’35W) (Dinsmore et al. 2010). Bedrock consists of

153 upper Carboniferous/lower Devonian sandstones with thin bands of limestone and coal horizons (Billett et al.
154 2004). These are overlain by fluvio-glacial, clay/silt-rich material, which in turn are overlain by peat deposits
155 (<0.5 m to 5 m thick) with increasing proportions of organo-mineral soils towards the catchment outlet (Billett
156 et al. 2004). Vegetation across the catchment is dominated by grasses and sedges (*Deschampsia flexuosa*,
157 *Molinia caerulea, Festuca ovina, Eriophorum angustifolium, Eriophorum vaginatum* and *Calluna vulgaris*)
158 covering a moss layer composed predominately of *Sphagnum* and *Polytrichum* spp. (Drewer et al. 2010). The
159 distinctive vegetation of the riparian zone is largely dominated by *Juncus effusus* associated with a moss-rich
160 base layer. Auchencorth Moss is predominantly used for low density (less than one livestock unit per hectare)
161 sheep grazing throughout the year (Drewer et al. 2010). Historic, >100 year old, regularly spaced drainage
162 ditches are present but are largely overgrown and terminate approximately 20 m before the start of the riparian
163 zone.

164 For the purposes of this study the riparian zone is defined as a 1-5 m wide corridor immediately adjacent to the
165 stream channel which is periodically inundated by the stream and easily identifiable by a break in slope (~ 80
166 cm below the level of the surrounding peat). The riparian zone is characterised by distinctive soil and vegetation
167 types and has higher than average water tables. The soils within the riparian zone contain re-worked peat inter-
168 bedded with cm scale sand/clay horizons deposited during periods of overbanking (details below).

169 The catchment is drained by the Black Burn, a small (mean width 68 cm; Billett and Harvey 2013), turbulent,
170 first order stream with low pH (mean pH 5.5) which displays a flashy response to rainfall events. Daily mean
171 discharge at the catchment outlet ranges between 0.95 and 1815 L s^{-1} with a median of 25.9 L s^{-1} (Dinsmore et
172 al. 2013).

173 Previous studies at the site have characterised the isotopic composition of DOC and CO_2 dissolved in stream
174 water and CO_2 evasion from the stream surface (Billett et al. 2006, 2007; Garnett et al. 2012c). Garnett and
175 Billett (2007) analysed the isotopic composition of riparian plants, but these are the first soil samples collected
176 at the site.

177 2.2 Field procedures

178 Sampling was carried out during two campaigns in 2012, 5th April - 3rd May and 22nd August - 18th September
179 with the sampling periods hereafter referred to as 'April' and 'September' respectively. The two time periods
180 were chosen to represent contrasting seasons with April having cool, low productivity and dry antecedent

conditions, whilst in September temperatures were higher, with greater catchment productivity and wet antecedent conditions (Table 1). All sampling was carried out along a 10 m long transect connecting the peatland, riparian zone and stream sampling points (Figure 1).

Soil cores were collected in both the peatland and riparian zone using a 6 cm diameter gouge type soil auger. Five × 5 cm thick slices were taken from each core for isotope analysis. Both peatland and riparian cores were sampled at depths of 5-10 cm, 25-30 cm, 45-50 cm and 65-70 cm; the deepest sampling point for the peatland and riparian cores were 145-150 cm and 75-80 cm, respectively, representing the depth of transition between the peat and underlying fluvio-glacial material. The sampling depths were selected to best capture each of the identified soil horizons from soil pits which were dug in both the peatland and riparian zones. From each identified horizon soil was collected in triplicate 100 cm^3 metal rings to determine soil bulk density, carbon content and pH.

Probes for sampling soil gases consisted of a length of stainless steel tubing (outer diameter 6 mm) with a 5 cm long sampling window covered by a gas permeable, hydrophobic membrane (Accurel PP V8/2 HF, Membrana GmbH, Germany) and were installed within both the peatland and riparian zone following the method of Garnett et al. (2011). A total of 4 probes were installed at both sites comprising three replicate probes with sampling windows at a depth of 40-45 cm, and one probe with a sampling window at 65-70 cm (Figure 1). Probes were installed two weeks prior to sample collection so the small probe headspace volume (<8.8 mL) would become equilibrated with the soil. For sample collection, glass flasks (volume ~215 ml) evacuated to a high vacuum ($<10^{-2}$ mB) were attached to the ends of the stainless steel probes via PVC tubing (Tygon, Fisher, UK). Flasks were left in place for four weeks. Due to probe failure only two shallow riparian CO_2 and CH_4 replicates were collected in April.

Soil water for DOC analysis was collected from a sampling probe installed in the shallow and deep depths of both the peatland and riparian zone. The design was similar to that of the gas probes but instead of the gas permeable, hydrophobic membrane the sampling window consisted of a number of small incisions made into the stainless steel tubing to allow water ingress. Glass vacuum flasks were only deployed for a period of 24 hours for soil water collection.

Samples of CO_2 and CH_4 emitted from the peatland and riparian surface were collected from static chambers following the method of Garnett et al (2012b). Chamber design was based on that of Dinsmore et al. (2009) and Drewer et al. (2010). A chamber was installed in the peatland and riparian zone each consisting of an opaque

polypropylene flange (40 cm diameter) inserted into the ground to a depth of approximately 15 cm; chamber bases were installed seven weeks prior to sampling and left *in-situ* for the duration of the study. Extension sections of 25 cm height, made from the same opaque polypropylene as the bases, were placed onto the bases and the chambers closed with a solid metal lid. Two auto shutoff Quick Coupling sampling points were installed in the chamber lid (Colder Products Company, USA) with one used for sample collection and the other opened to the atmosphere to equilibrate pressure within the chamber during sampling. Chamber volumes were 32 L and 50 L for peatland and riparian zone, respectively.

Static chambers were closed for a period of 5-9 days to allow sufficient concentrations of CO_2 and CH_4 to build up. For routine ^{14}C analysis a minimum sample size of ~1 mg C was required. Using this value the minimum concentration within the chamber and required sample volume were calculated. CH_4 concentration was the limiting factor due to fluxes being considerably lower than for CO_2. Changes in chamber CO_2 and CH_4 concentrations over the enclosure period were monitored by periodically collecting and analysing 100 ml subsamples by gas chromatography at CEH Edinburgh. When chamber CH_4 concentration reached 100 ppmv gas samples were collected in 10 L foil bags (SKC Ltd, UK) using a battery powered pump with a flow rate of ~1 L min^{-1}. To collect sufficient sample in the riparian zone in April, when concentrations stabilised at 25 ppmv, five foil bags were collected over a series of days to prevent over extraction of the chamber volume and the drawing up of soil gases.

To collect the gas evaded from the stream surface a floating chamber was installed on the Black Burn (Garnett et al. 2012c). The floating chamber (surface area ~1,500 cm^2, volume 42 L) was constructed from the bottom section of a barrel ('Open top keg', Ampulla Ltd, UK). To increase the buoyancy a ring of plastic and pipe lagging was placed around the chamber at water level. The chamber was secured in place using two, 1.5 m length (10 mm diameter) stainless steel rods secured into the stream bed. The chamber was connected to these rods using stainless steel saddle clamps (RS Components, UK) to allow it to rise and fall with changes in stream level. The chamber was installed and allowed to equilibrate for 24 hours prior to sampling. An auto shutoff Quick Coupling sampling point on the top of the chamber allowed the removal of chamber gas to a foil gas bag using a pump as described above (a second sampling point was opened during sampling to act as a vent by which atmospheric equilibrium was maintained). Stream water DOC was collected by filling a 300 ml glass bottle.

2.3 Laboratory procedures

239 The outer 1 cm of the soil core sections was removed before processing to avoid potential contamination from
240 smearing of peat material from higher in the soil profile during sampling. The remaining soil sample was then
241 homogenised and a sub-sample sent to the NERC Radiocarbon Facility (RCF) for further analysis. No pre-
242 treatment to remove mobile fractions from the soil was carried out. The soil was dried and then combusted to
243 CO_2 using an elemental analyser and converted to graphite by Fe/Zn reduction (Slota et al. 1987).

244 Soil was analysed for dry bulk density by drying for 24 hours at 106 °C. Samples were then combusted for 16
245 hours at 375 °C to determine the %organic carbon content by loss on ignition (Ball, 1964). Soil pH was
246 measured in a mixture of two parts deionised water to one part fresh peat using a MP220 pH meter (Mettler
247 Toledo, UK).

248 The glass flasks containing the soil atmosphere samples and the foil gas bags containing the chamber samples
249 were returned to the RCF and separated into their CO_2 and CH_4 components. The glass flask samples were
250 separated using the method of Garnett et al. (2011). Firstly the CO_2 component was trapped on a molecular
251 sieve cartridge with the remaining CO_2-free CH_4 sample combusted to CO_2 by passing over platinum-
252 aluminium beads at 950 °C in an atmosphere of excess oxygen. The CH_4 derived CO_2 was then cryogenically
253 purified using a slush trap (mix of dry ice and ethanol at -78 °C) to remove water and then liquid nitrogen (-196
254 °C) to separate CO_2 from other gases. Finally the CO_2 sample was recovered from the molecular sieve cartridge
255 by heating (500 °C) while attached to a vacuum rig (Garnett and Murray, 2013). For the foil bags a subsample
256 of the contents was taken and the CO_2 component isolated by cryogenic purification. The CH_4 component was
257 isolated from the remaining sample as described for the flask samples above.

258 Water samples were filtered through 0.7 μm GF/F filter papers (Whatman, UK), which had been pre-combusted
259 at 500 °C for 5 hours prior to use (Chanton et al. 2008). Samples were returned to clean glass bottles and stored
260 in the dark at 4 °C before being passed to the RCF. Each sample was then acidified to pH 4 and sparged with N_2
261 gas for 20 mins. After the pH had been returned to pH 7 a measured volume was removed for rotary
262 evaporation. After freeze drying the sample was converted to CO_2 by combustion in an elemental analyser and
263 converted to graphite by Fe/Zn reduction (Slota et al. 1987).

264 For each sample, $\delta^{13}C$ (relative to the Vienna Pee Dee Belemnite standard) was determined on a dual inlet
265 isotope ratio mass spectrometer (Thermo Fisher Delta V). In the five instances where there was insufficient
266 sample for a separate $\delta^{13}C$ measurement (* in Appendix 1) this was performed by AMS at the same time as ^{14}C
267 measurement. ^{14}C was determined at the Scottish Universities Environmental Research Centre (SUERC)

accelerator mass spectrometry (AMS) facility. Results are reported following radiocarbon conventions as both %modern and conventional radiocarbon age (years BP) where applicable, with ±1σ analytical precision and were normalised to a $\delta^{13}C$ of -25 ‰ to account for mass-dependent fractionation. The five samples requiring 'small sample' AMS analysis have a greater analytical uncertainty for both ^{14}C and $\delta^{13}C$ (Appendix 1).

2.4 Data analysis

As no attempt was made to remove atmospheric CO_2 or CH_4 from the chambers prior to sampling, a mass balance approach was used to remove their contribution to the isotope results. For CO_2 the assumed atmospheric composition in the chamber prior to sampling was 390 ppmv with a ^{14}C concentration of 103.7 %modern and $\delta^{13}C$ of -9 ‰ (Levin et al. 2008). Atmospheric CH_4 was removed from the CH_4 isotope results assuming a concentration of 2 ppmv, a ^{14}C content of 130 %modern and a $\delta^{13}C$ of -47 ‰ (Lassey et al. 2007).

Where data from the replicate samples (n=3) have been summarised the arithmetic mean and the standard error of the mean were calculated. To test for statistical differences between peatland and riparian zones a Student's t-test was performed for the soil profiles and ANOVA to test for differences in the soil gas replicates. The standard deviation was also calculated for the replicates to determine the precision of the results.

An isotope mass balance approach (Equation 1) (Chaser et al. 2000) was used to estimate the fraction (f) of carbon from different sources within samples of soil DOC, CO_2 and CH_4 and evasion CO_2 and CH_4. $\Delta^{14}C_{meas}$ is the measured ^{14}C content of the sample and $\Delta^{14}C_{mod}$ is the atmospheric ^{14}C content of carbon fixed by plants during 2012 estimated at 103.7 %modern (Levin et al. 2008). To estimate the contribution from soil ($\Delta^{14}C_{soil}$), measured ^{14}C values from this study were used. To determine the fraction of geogenic derived carbon from bedrock sources, $\Delta^{14}C_{geo}$ value of 0 %modern (i.e. of sufficient age that no measureable ^{14}C remains) was used in place of $\Delta^{14}C_{soil.}$

Equation 1 $$\Delta^{14}C_{meas} = (f)(\Delta^{14}C_{mod}) + (1 - f)(\Delta^{14}C_{soil})$$

Local meteorological data over the full year 2012 were provided from the European Monitoring and Evaluation Programme (EMEP) flux tower located ~1 km from the transect and were used to aid the interpretation of results. Data on background carbon concentrations and fluxes and hydrological conditions including water table, soil water temperature and stream discharge are from Leith et al. (in prep).

295 3 Results

296 3.1 Hydrology and meteorology

297 Total rainfall for 2012 was 1237 mm, 7 % higher than the 2002 - 2008 average of 1055 mm (Drewer et al. 2010)
298 but with an uneven distribution across the year (Leith et al. in prep); 32 % of the total annual rainfall fell in June
299 and July. In the April sampling period there was a total of 90.1 mm of rainfall with a lower total of 78.4 mm in
300 September. Average air temperature during the September sampling period was 11.1 °C compared with 4.9 °C
301 in April; stream water temperature was also higher during the September sampling period (Table 1). Average
302 water table depths in the peatland were the same in both sampling periods (-30 cm) but with a larger range in
303 April (-60 to -7 cm) compared to September (-47 to -8 cm). Water tables were higher in the riparian zone with
304 means of -17 cm in April and -22 cm in September (Figure 2). Greater rainfall in April meant that mean
305 discharge was greater (42.0 L s^{-1}) compared to September (25.3 L s^{-1}) (Table 1). However, when samples for
306 DOC and evasion CO_2 and CH_4 were collected stream discharge was relatively stable and similar (11.3 and 13.9
307 L s^{-1}, respectively).

308 Antecedent conditions in the three months prior to sampling varied considerably between the two periods. In
309 April the preceding three months were characterised by dry weather with low discharge whereas in September
310 the three months before sampling were extremely wet with consistently high discharge. A number of
311 overbanking events occurred throughout the year, shown by above ground surface water table positions in the
312 riparian zone (Figure 2). The two largest of these, which occurred in the summer period between the two
313 sampling occasions, flooded the entire riparian zone with noticeable amounts of stream sediment, consisting of
314 peat and sandy material, deposited onto the surface of the riparian zone.

315 3.2 Soil

316 Peatland and riparian soil profiles differed despite the two sites being only 10 m apart (Figure 3). The peatland
317 profile contained five organic horizons (O1-5) with varying levels of decomposition. Two horizons (O2, O4)
318 contained abundant poorly decomposed graminoid plant fragments, while horizons O3 and O5 were
319 characterised by highly humified peat. The O2 and O4 horizons contained the most abundant plant fragments
320 and had lower bulk density, 0.10 and 0.11 g cm^{-3}, compared with the more humified horizons O3 and O5. The
321 organic carbon content of the soil was relatively low (30.7-39.3 %) suggesting a component of mineral soil
322 within the peat (Table 2).

323 The riparian profile contained three organic horizons (O1-3) with a continuous sand layer (C1) at 60 cm
324 marking the boundary between the overlying peat and a deeper horizon with broken and contorted sandy lenses
325 (C2), which in turn overlaid the fluvio-glacial horizon (Figure 3). The transition was also marked by a large
326 increase in the bulk density from 0.14-0.35 g cm^{-3} in the organic horizons to 0.86 g cm^{-3} in the sand-rich horizon
327 (Table 2). This horizon contained much less organic carbon (5.2 %), compared with organic layers above (18.1
328 to 28.4 %). All horizons in the riparian zone contained less organic material compared to the peatland where
329 organic carbon content ranged from 30.7-39.3 %C; soil pH was also lower in the peatland soils (Table 2). The
330 irregular decrease in carbon content with depth and the presence of sandy horizons are characteristic of fluvisols
331 (Figure 3).

332 In both the peat and riparian zone soils the O1 horizon was poorly decomposed and contained abundant roots
333 and plant litter. The extent of this layer and the composition of the plant material varied between the sites with
334 graminoid remains in the peatland and a thicker layer of *Juncus effusus* roots in the riparian zone. Active rooting
335 depth was ~25 cm in both soil types.

336 Peatland soil age increased with depth from 134 ± 37 years BP at 5-10 cm depth (O1-O2 horizons) to 665 ± 37
337 years BP at the basal depth (O5) (Figure 4, with details in Appendix 1). The age at 25-30 cm (O3) did not fit this
338 age-depth profile, being considerably older at 947 ± 41 years BP. The riparian soil profile was significantly
339 older than the peat (T= -2.95 P= 0.02) ranging from 759 ± 37 years BP at 25-30 cm depth (O2) to 1407 ± 36
340 years BP at 65-70 cm depth (C2). Neither the peatland nor riparian zone soil profiles displayed a linear increase
341 in age with depth, which is typical in most peats. No significant differences existed in peatland and riparian
342 $\delta^{13}C$, with all values in the range of -26.7 to -29.9 ‰.

343 3.3 Porewater DOC, CO_2 and CH_4

344 DOC, CO_2 and CH_4 in peatland porewater were consistently >100 %modern (Figure 5) (Appendix 1). The
345 riparian zone also had ^{14}C values predominantly >100 %modern, but with three exceptions. Aged CH_4 was
346 found at 70 cm in the riparian zone in April (81 ± 77 years BP) with riparian porewater DOC in September
347 having a radiocarbon age of 327 ± 37 years BP at 45 cm depth and 117 ± 37 years BP at 70 cm depth. Porewater
348 DOC, CO_2 and CH_4 were all significantly younger than the surrounding soil material; which at equivalent
349 depths were 459 ± 37 and 552 ± 35 years BP in the peatland and 933 ± 37 and 1407 ± 36 years BP in the
350 riparian zone.

Across the sampling periods, $\delta^{13}C$ values for porewater CO_2 had mean values of -7.4 ‰ in the deep peat and -14 ‰ in the deep riparian zone, whereas porewater CH_4 had mean values of -76.4 and -73.2 ‰ in the peatland and riparian zone, respectively. CO_2 was enriched in ^{13}C and CH_4 depleted in ^{13}C, relative to soil material which ranged from -26.7 to -29.9 ‰. $\delta^{13}C$ values for porewater DOC had a narrower range in April (-27.5 to -28.2 ‰) and September (-27.6 to -27.9 ‰). ^{14}C concentrations were similar between the different carbon species but the wider range of ^{13}C values resulted in different carbon species having distinct clusters (Figure 5).

No significant differences occurred in the ^{14}C content of porewater CO_2 or CH_4 between the peatland and riparian zone in either April or September. Significant differences existed in April for both $\delta^{13}CH_4$ ($F=16.5$, $P<0.05$) and $\delta^{13}CO_2$ ($F=198$, $P<0.01$) with the riparian porewater ^{13}C depleted in both CH_4 and CO_2 relative to the peatland. In September there were no significant differences between the peatland and riparian porewater for either $\delta^{13}CH_4$ or $\delta^{13}CO_2$. There was good agreement between the three replicates of $^{14}CO_2$ in the peatland with mean ± standard deviation of 103.66 ± 0.46 %modern and 104.58 ± 0.81 %modern in April and September, respectively. There was greater variability in the riparian zone with values of 104.51± 1.63 %modern (April) and 103.17 ± 1.58 %modern (September).

3.4 Soil surface emissions

Gaseous carbon emissions from the surface of the soil were all >100 %modern (Figure 6, Appendix 1). CO_2 emissions from the peatland were enriched in ^{14}C (104.79 and 105.70 %modern in April and September) relative to the contemporary atmosphere (103.7 %modern in 2012) while the riparian emissions were depleted (100.59 and 100.99 %modern in April and September). Based on comparisons with the atmospheric $^{14}CO_2$ record of Levin et al. 2008, the $^{14}CO_2$ results suggest that CO_2 emitted from the peatland surface in 2013 was on average fixed from the atmosphere between about 2007 and 2010.

Emitted CH_4 was consistently more enriched in ^{14}C from the peatland (107.29 and 108.25 %modern in April and September) than the riparian zone (101.79 and 104.84 %modern). Overall, emissions in both the peatland and riparian zone were more ^{14}C enriched in September than April. All emissions were significantly enriched relative to the age of soil material which at 5-10 cm depth had radiocarbon ages of 134 ± 37 and 1107 ± 37 years BP in the peatland and riparian zone, respectively.

$\delta^{13}C$ values for CO_2 emitted from the peatland and riparian zone had a narrow range (-25.9 to -27.1‰) with values more depleted in September than April (Figure 6). CH_4 had a larger range of $\delta^{13}C$ values across the

379 measurement periods between -63.2 and -58.0 ‰ (peatland) and -75.9 and -63.5 ‰ (riparian). $\delta^{13}CH_4$ values
380 were more enriched in September than April, the opposite pattern found for CO_2 (above).

381 3.5 Stream evasion and DOC export

382 Evasion was depleted in ^{14}C relative to soil emissions suggesting a contribution from aged carbon. Evaded CO_2
383 had radiocarbon values of 36 ± 37 years BP and modern and evaded CH_4 was aged 537 and 310 ± 38 years BP
384 in April and September respectively (Appendix 1). Evaded CO_2 in April (-17.4 ‰) was ^{13}C-enriched compared
385 to September (-20.5 ‰). CH_4 was ^{13}C-depleted, with values of -58.1 ‰ and -54.3 ‰ in April and September
386 respectively (Figure 6).

387 Stream water DOC showed the largest range in ^{14}C ranging from 100.41 %modern in April to 106.47 %modern
388 in September. The more enriched value in September was opposite to the pattern seen for soil DOC. No
389 significant differences were seen in $\delta^{13}C$, with values of -28.7 ‰ in both sampling periods (Figure 6).

390 4 Discussion

391 4.1 Composition of terrestrial carbon pools

392 The composition and depth of the soil profiles were considerably different in the peatland and riparian zone
393 (Figure 3). Riparian soils were characterised by sandy horizons (C1 and C2 horizons), higher bulk density and
394 an irregular decrease in % C with depth (Table 2) indicating the deposition of eroded and reworked peat and
395 mineral material during periods of overbanking. Dense vegetation on the surface of the riparian zone is likely to
396 contribute to the trapping of sediment transported by flood waters (Evans and Warburton 2005). The complete
397 vegetation cover will also minimise the erosion of soil horizons; suggesting that deposition rather than erosion is
398 creating the riparian soil profile. Despite the peatland being only 10 m from the stream, it is approximately 80
399 cm higher than the adjacent riparian zone and whilst the riparian zone was inundated on several occasions
400 during this study, no flood events high enough to reach the peatland were recorded in the period July 2011 to
401 February 2013.

402 The soil isotopic data showed the riparian zone to be considerably older (759-1407 years BP) than the peatland
403 (134-947 years BP) (Figure 4), possibly reflecting the input of older stream sediment from overbanking events.
404 This is in agreement with Palmer et al. (2001), the only other study we are aware of to determine the isotopic

405 composition of both peatland and riparian soils. The $\delta^{13}C$ values cover a narrow range from -26.7 to -29.9 ‰
406 indicating C3 plant material was the primary source of carbon in both peatland and riparian soils.

407 No clear age/depth relationship was observed in the riparian zone (Figure 4) highlighting the complexity of
408 riparian zone soil formation. In the peatland profile, ^{14}C age increased with depth (with the exception of the
409 point at 25 cm depth) and our data suggest a high peat accumulation rate. The anomalous age at 25-30 cm depth
410 could be due to the deposition of soot particles (Charman and Garnett 2005), historical additions of soil
411 improvement materials containing $CaCO_3$, or a large flood event. The peatland site is also on the edge of the
412 peatland plateau in comparison to other studies which have dated soil cores in more stable areas in the centre of
413 the peatland (Aravena et al. 1993; Charman et al. 1999; Clymo and Bryant 2008).

414 Since it was our intention to take a snapshot of the ^{14}C in the total soil C pool it was not appropriate to perform a
415 pre-treatment of the soil samples, as would normally be undertaken when deriving a chronological record using
416 radiocarbon analysis. As a result, mobile fractions would have been included within the samples, as would the
417 presence of any mineral soil material, especially carbonates or coal fragments. The high apparent accumulation
418 rate is likely to be a result of the composition of the peat, which contains poorly decomposed graminoid plant
419 material to a depth of 80 cm, plus the transport of young mobile fractions, such as root exudates or DOC, down
420 the soil profile.

421 Soil gases in both the peatland and riparian zone were generally >100 %modern; CO_2 ranged from 100.73 to
422 105.66 %modern and CH_4 from 99.00 to 105.46 %modern, with values becoming more ^{14}C depleted with depth.
423 The results are in agreement with other studies which measured the isotopic composition of soil gases in
424 peatlands, with modern CO_2 found at 30 cm (Billett et al. 2012) and modern CH_4 at 50 cm depth (Clymo and
425 Bryant 2008). Only one sample (deep riparian CH_4 in April), was <100 %modern. This contrasts with other
426 studies which have widely found aged carbon at depth, with CO_2 98.79-94.58 %modern at 50-100 cm depth
427 (Billett et al. 2012; Clymo and Bryant 2008) and CH_4 97.30-77.30 % modern at 25-100 cm depth (Garnett et al.
428 2011).

429 Consistent with other studies (Charman et al. 1999; Clymo and Bryant 2008, Chanton et al. 2008) soil gases
430 were consistently younger than the surrounding soil material at both sampling depths in both the riparian zone
431 and the peatland. Isotope mass balance indicates that soil organic matter only contributed 1-5 % of CO_2 and CH_4
432 at 40-45 cm rising to 5-24 % at 65-70 cm. The remainder is likely to be derived from recently fixed carbon
433 derived from either the downward transport of young CO_2 and CH_4 from the surface or infiltration of DOC

down the soil profile providing the substrate for fermentation and methanogenesis (Aravena et al. 1993; Corbett et al. 2013). The similarity in ^{14}C ages between CO_2 and CH_4 suggests derivation from a single source, namely DOC transport down the soil profile (Clymo and Bryant 2008; Garnett et al. 2011).

Porewater DOC, with the exception of the riparian zone in September, was >100 %modern. Modern DOC at shallow depths has been found across a range of other peatlands (Chaser et al. 2000; Chanton et al. 2008) with transport of plant derived DOC from the surface down the soil profile shown to be the main process responsible for the presence of modern DOC at depth (Corbett et al. 2013). In September, the riparian zone displayed an age reversal with ^{14}C ages of 327 ± 37 years BP at 40-45 cm depth and 117 ± 37 years BP at 65-70 cm depth. The isotope mass balance indicated a 52 % contribution from soil at the shallow and 26 % at the deeper depths. During the three months prior to the September sampling period there were a large number of storm events (Figure 2), leading to overbanking and inundation of the riparian zone. During these events, peat and sandy material, most likely soil organic matter eroded from upstream areas, was deposited onto the surface of the riparian zone. We suggest that DOC was leached from this deposited peat material and transported vertically within the soil profile, explaining the presence of aged DOC in the riparian zone in September. While a number of storm events occurred in the three months preceding the April sampling period, none were sufficiently large to result in noticeable sediment deposition. This suggests that with the exception of large storm events, DOC is sourced predominantly from modern recently fixed carbon.

$\delta^{13}C$ values for both CO_2 and CH_4 were significantly different between the peatland and riparian zone sites in April but not in September. Differences in the methanogenic pathway (CO_2 reduction or acetate fermentation) calculated from carbon isotope fractionation (αC), calculated using the method of Whiticar et al. (1986), are reflected in values >1.065 indicating CO_2 reduction and values <1.055 indicating acetate fermentation (Conrad 2005). Peatland values (Table 3) were consistent with CO_2 reduction (average 1.072 across all samples) and were similar to the value of 1.075 found by Clymo and Bryant (2008). However, the riparian zone in September had lower αC values with two points suggesting a greater contribution from acetate fermentation as found in a number of other peatlands (Charman et al. 1999). It has been suggested by Sugimoto and Wada (1993) that acetate fermentation uses more labile carbon than CO_2 reduction (Chanton et al. 2008). Two potential processes responsible could be the input of labile root exudates at the end of the growing season in September associated with *Juncus effusus,* which was only found in the riparian zone, or the addition of carbon to the surface of the

riparian zone between April and September when overbanking occurred. Again this highlights the important role of stream processes in biogeochemical cycling within the riparian zone.

High analytical costs limit the number of samples that can be analysed for ^{14}C and restricts sample replication. Where replication has been included in studies (e.g. Clymo and Bryant 2008) variability between replicates of soil decomposition products has generally been small. This study, which was carried out in the dynamic peat margin and riparian zone also found good agreement between replicates. The riparian zone had greater variability in $^{14}CO_2$, with higher standard deviation than the peatland. The variability in the riparian zone can in part be due to the greater proportion of riparian samples analysed by small sample AMS, which had a larger associated uncertainty (Appendix 1). The same pattern was evident for $^{14}CH_4$ with greater variability in the riparian replicates compared with the peatland. Despite the slightly larger uncertainty in the riparian zone, the replication was generally very good across all samples highlighting the validity and reliability of the radiocarbon techniques used in this study.

4.2 Soil surface emissions

Soil surface emissions of CO_2 and CH_4 were all >100 %modern (Figure 6) and in line with the results from other studies (Chanton et al. 1995; Quay et al. 1991; Wahlen et al. 1989; Hardie et al. 2009). Emissions from the riparian zone were consistently depleted in ^{14}C relative to the peatland. The $\delta^{13}C$ values suggested a mixture of sources combining recently fixed carbon and a component of more ^{13}C depleted soil carbon. Hardie et al. (2009) partitioned total ecosystem respiration and found it to be composed of ~36 % soil respiration, 41-54 % from plant respiration and ~10-23 % from plant mediated transport from depth. Hornibrook (2009) showed that the transport mechanism between soils at <50 cm depth and the surface determines the $\delta^{13}C$ value of surface emitted CH_4. Figure 7 shows that the peatland soil emissions are most likely derived from diffusive transport through pore water, while in the riparian zone there is a component of active transport through plant aerenchyma. Preferential loss of $^{12}CH_4$ through the aerenchyma of graminoid plants results in more ^{13}C-enriched CH_4 (Hornibrook 2009). The riparian zone in the study site contains abundant *Juncus effusus* which is known to transport CH_4 through its aerenchyma facilitating transport from deeper soil layers (Dinsmore et al. 2009). Modern CO_2 and CH_4 were found at both sampling depths within the soil at Auchencorth Moss, suggesting that this porewater carbon is contributing to surface emissions.

The build up of CO_2 and CH_4 in the chamber headspace during the long (5-9 day) chamber closure period is likely to have had an impact on the soil-atmosphere diffusion gradient, and hence on the flux rate (Davidson et al. 2002). Over the closure period, the rate of concentration increase within the chamber began to slow after ~24 hours but did not level off over the ~5 days prior to sampling. It is unlikely that the carbon isotope results were affected by this slowing of the diffusion gradient (Garnett et al. 2012b). Furthermore, given the cool mean air temperatures in April (4.9 °C) and September (11.1 °C), there was no observed vegetation die back in the chambers, which would have altered the balance of soil and plant respiration. Ebullition is unlikely to be significant at this site as soil CH_4 concentrations were consistently less than the minimum concentration (~8.0 mg CH_4 L^{-1}) required for bubble formation (Baird et al. 2004). We therefore conclude that our results are a good representation of the isotopic composition of bulk respiration from the peatland and riparian zone.

4.3 Export via the aquatic pathway

DOC in stream water was modern but with a greater enrichment of ^{14}C in September. This finding is consistent with the results from many other studies which determined the dual isotope composition of DOC in peatland headwater streams (Billett et al. 2007, 2012; Schiff et al. 1997). In-stream processing would lead to DOC becoming more ^{13}C enriched (Billett et al. 2012), however the consistency of $\delta^{13}C$ between the sampling periods in the stream and the similarities between soil and stream DOC, suggests there was very little in-stream processing at the site. This supports the conclusions of other studies such as Dinsmore and Billett (2008) who attributed aquatic carbon in the same study stream to allochthonous sources rather than in-stream processing.

Evaded CO_2, which had ^{14}C values of 98.36 and 101.35 %modern, was within the range of 83.52-107.00 %modern found across a range of peatland catchments (Billett et al. 2007; Garnett et al. 2012c). The results were however considerably younger than previous studies which determined the isotopic composition of evasion and dissolved CO_2 ~800 m downstream of the site used in this study. Billett et al. (2006) reported evasion ^{14}C ages of up to 1454 years BP, and Garnett el al. (2012a) measured dissolved CO_2 concentrations in the range 707-1210 years BP.

CH_4 evasion was considerably older than evaded CO_2 with ages of 537 ± 38 years BP in April and 310 ± 38 years BP in September. This was younger than the results from Garnett et al. (2012c), the only other study to measure the $^{14}CH_4$ content of evasion, who reported ages in the range 1617-1987 years BP at another Scottish

peatland site. Evaded CO_2 and CH_4 were depleted in ^{14}C relative to the soil gases, which were predominantly modern, indicating contributions form an additional ^{14}C depleted source.

CO_2 from carbonate weathering and CH_4 from coal seams, both of which occur in the catchment bedrock (Billett et al. 2004), may contribute additional geogenic carbon. These geogenic sources will contribute to stream water via deeper hydrological flowpaths and will be ^{14}C dead (i.e. of sufficient age that no measureable ^{14}C remains). They therefore have the potential to significantly shift the isotopic signature while only contributing small amounts of carbon. Near-surface hydrological flowpaths, at similar depths to where the porewater isotopic measurements were made, were found to consist predominantly of modern, plant derived carbon (Figure 5). Mass balance using the isotopic composition of atmospheric CO_2 in 2012 (^{14}C = 103.7 %modern; $\delta^{13}C$ = -9 ‰) and geogenic carbon (^{14}C = ~0 %modern; $\delta^{13}C$ = ~0 ‰) indicates a contribution up to 5 % and 28 % for $^{14}CO_2$ and $\delta^{13}CO_2$, respectively, similar to the ~21 % and 30 % calculated by Billett et al. (2007). The younger radiocarbon age for CO_2 evasion than reported downstream (Billett et al. 2006; Garnett et al. 2012a) may therefore be explained by a lesser contribution from geogenic carbon inputs at our upstream site highlighting spatial variability in sources along the stream length. The mass balance also suggests a greater contribution from geogenic CH_4 sources to the isotopic composition of evasion $^{14}CH_4$ (27 %) than for $^{14}CO_2$ (5 %). Another source of aged CH_4 could be deep peat derived CH_4, as suggested by Garnett et al. (2012c). While measured porewater CH_4 was generally modern, peat up to 5 m depth occurs upstream in the catchment, which may contribute an unmeasured source of old deep peat derived CH_4. The results suggest that unmeasured sources (including deeper soil carbon and geogenic inputs) are contributing to evasion but overall, modern, plant derived carbon is the predominant component.

4.4 The role of the riparian zone

Differences in the soil physical properties and the ^{14}C content between the peatland and riparian zone can be linked to the deposition of reworked peat material onto the surface of the riparian zone during overbanking events. This results in the peatland and riparian zone, despite only being 10 m apart, being distinct biogeochemical environments. An increase in the frequency and intensity of storms, which is expected under current climate change predictions (Pachauri and Reisinger 2007), could lead to an increase in the rate of sediment deposition making the riparian carbon cycle particularly sensitive to climate related changes.

The isotope results from this study highlight some of the differences in carbon dynamics within the peat-riparian-stream continuum. The different $\delta^{13}CH_4$ signatures between the peatland and riparian areas indicate not

547 only the varying carbon dynamics involved in the production of CO_2 and CH_4 within the soil profile, but also
548 the transport mechanism by which these gases reach the soil surface. Additionally, aged DOC was only found in
549 the riparian zone after overbanking events occurred, suggesting that carbon within the deposited sediment is
550 labile and readily incorporated into the soil or converted to DOC, CO_2 or CH_4. This highlights the important role
551 that depositional processes have on the isotopic signature of soil and soil gases within the riparian zone.

552 The results of this study suggest that deeper peat layers contribute only a small proportion to stream and soil
553 surface emissions, unlike degraded peatlands (Moore et al. 2013). Evasion, which was the only pathway to have
554 an isotopic signature indicating a component of aged carbon, consisted predominately of modern soil derived
555 CO_2 and CH_4 but with a component from geogenic sources of up to 5 % for CO_2 and 28 % for CH_4. This
556 suggests that the stream bed may be acting as a pathway by which carbonate weathering derived CO_2 and deep
557 geologically derived coal bed CH_4 can be released. Gaseous carbon exported via the stream is therefore a more
558 complex mix of sources than emissions from the soil surface. Despite the aged DOC found in the riparian zone,
559 stream water DOC was consistently modern, again suggesting that the riparian zone is not a major contributor of
560 carbon to the stream.

561 The overall prevalence of modern carbon shows that the carbon cycle in this peatland predominately involves
562 modern, recently fixed carbon in agreement with studies which find Auchencorth Moss to be a net sink of
563 carbon and in an actively aggrading state (Dinsmore et al. 2010, 2013).

564

565 5 Conclusions

566 The soil characteristics and isotopic composition of soil and its decomposition products are distinctly different
567 in the riparian zone and the peatland. Soil was older in the riparian zone (1055 ± 107 years BP) than in the
568 peatland (551 ± 133 years BP). These results suggest that the deposition of stream sediment onto the riparian
569 zone and the rapid processing of this carbon is an important carbon source to the riparian zone and is likely to be
570 the process responsible for many of the differences observed between the peatland and riparian zone.

571 Despite the importance of hydrochemical interactions between the stream and riparian zone the relationship
572 does not appear to be reciprocal for peatland carbon. The isotopic composition of stream water was different to
573 that found in the riparian zone with evasion containing carbon from elsewhere in the catchment with a possible
574 contribution from geogenic sources of up to 5 % for CO_2 and 28 % for CH_4. Despite the aged DOC found in the

riparian zone in September, stream water DOC was consistently modern, again suggesting that the riparian zone is not a major contributor of carbon to the stream.

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Table 1 Mean and (min – max) of water temperature (measured in either dipwells or the stream channel) and water table depth. Discharge is the mean ± SE as range was fixed (0.28 to 290 Ls $^{-1}$). Values are calculated for April and September sampling periods and for the whole of 2012

Sampling Period	Site	Temperature (ºC)	Water table (cm)	Discharge (L s^{-1})
April	Peatland	6.1 (6.0 – 6.3)	-30 (-59 to -6)	
	Riparian	5.8 (5.6 – 6.0)	-17 (-46 to +6)	
	Stream	5.5 (0.6 – 9.6)		42.0 ± 1.3
September	Peatland	11.5 (11.0 – 12.3)	-30 (-47 to -8)	
	Riparian	11.1 (10.7 – 11.4)	-22 (-47 to +46)	
	Stream	11.7 (6.7 – 16.3)		25.3 ± 1.1
Annual	Peatland	7.1 (3.5 – 11.4)	-31 (-90 to -2.3)	
	Riparian	7.1 (3.0 – 12.3)	-19 (-90 to +50)	
	Stream	6.9 (-3.9 – 25.8)		48.6 ± 0.5

Table 2 Soil properties for the horizons shown in Figure 3. No samples were collected from the riparian C1 horizon and the peatland O1 horizon as they were too thin for sample collection

Soil	Horizon	Bulk density (g cm^{-3})	pH	% OC
Riparian	O1	0.14	4.0	28.4
	O2	0.35	4.5	18.1
	O3	0.31	4.2	26.8
	C1	/	5.3	/
	C2	0.86	5.7	5.2
Peatland	O1	/	4.0	/
	O2	0.10	3.9	30.7
	O3	0.14	3.9	33.0
	O4	0.11	4.2	39.3
	O5	0.18	4.6	34.6

Table 3 αC values for the soil gases. [a] indicates CO_2 reduction and [b] acetate fermentation as the likely production pathway based on Whiticar et al. (1986).

Site	Sample type	April αC	September αC
Peatland	Soil (40-45cm)	1.072[a]	1.071[a]
	Soil (40-45cm)	1.075[a]	1.060[a]
	Soil (40-45cm)	1.072[a]	1.066[a]
	Soil (65-70) cm	1.075[a]	1.074[a]
Riparian Zone	Soil (40-45cm)	/	1.047[b]
	Soil (40-45cm)	1.073[a]	1.061[a]
	Soil (40-45cm)	1.078[a]	1.046[b]
	Soil (65-70) cm	1.066[a]	1.056[a]

Appendix 1 All radiocarbon data from this study. SPa-c refer to the replicates at the shallow depth in the peatland; SRa-c refers to replicates at the shallow depth in the riparian zone. * indicates insufficient sample collected for routine ^{14}C analysis so small sample AMS used with $\delta^{13}C$ determined online by the AMS

Sample	Publication Code (SUERC-)	^{14}C Enrichment (%modern ± 1 σ)	Radiocarbon age (years BP ± 1 σ)	$\delta^{13}C$ (± 0.1 ‰)
Soil				
Peat (5-10 cm)	40585	98.34 ± 0.45	134 ± 37	-27.9
Peat (25-30 cm)	44328	88.88 ± 0.45	947 ± 41	-26.7
Peat (45-50 cm)	40586	94.45 ± 0.43	459 ± 37	-27.4
Peat (65-70 cm)	44329	93.36 ± 0.41	552 ± 35	-29.9
Peat (145-150 cm)	40587	92.05 ± 0.42	665 ± 37	-28.5
Riparian (5-10 cm)	40588	87.13 ± 0.40	1107 ± 37	-27.0
Riparian (25-30 cm)	44330	90.98 ± 0.42	759 ± 37	-27.6
Riparian (45-50 cm	40589	89.03 ± 0.41	933 ± 37	-27.8
Riparian (65-70 cm)	44331	83.93 ± 0.37	1407 ± 36	-27.6
Riparian (75-80 cm)	40590	87.53 ± 0.40	1070 ± 37	-28.0
Soil CO_2				
Apr - SPa - CO_2	40571	103.40 ± 0.47	Modern	-12.0
Apr - SPb -CO_2	40575	104.19 ± 0.48	Modern	-12.0
Apr - SPc - CO_2	40577	103.39 ± 0.47	Modern	-11.0
Apr - DP - CO_2	44297	102.90 ± 0.48	Modern	-7.8
Apr - SRb - CO_2	40578	103.36 ± 0.47	Modern	-19.8
Apr - SRc - CO_2	40579	105.66 ± 0.45	Modern	-21.0
Apr - DR - CO_2	44298	101.22 ± 0.45	Modern	-15.2
Sept - SPa-CO_2	44299	105.02 ± 0.49	Modern	-11.0
Sept - SPb-CO_2	44300	103.65 ± 0.48	Modern	-17.4
Sept - SPc-CO_2	44301	105.07 ± 0.49	Modern	-10.7
Sept - DP-CO_2	44304	102.58 ± 0.45	Modern	-6.9
Sept - SRa-CO_2	44305	103.36 ± 0.48	Modern	-16.0
Sept - SRb-CO_2	44306	101.50 ± 0.51	Modern	-14.3
Sept - SRc-CO_2	44307	104.67 ± 0.49	Modern	-17.1
Sept - DR-CO_2	44308	100.73 ± 0.47	Modern	-13.2
Soil CH_4				
Apr - SPa – CH_4	40570	104.51 ± 0.48	Modern	-78.4
Apr - SPb –CH_4	40572	104.25 ± 0.45	Modern	-81.3
Apr - SPc - CH_4	40576	104.41 ± 0.45	Modern	-77.5
Apr - DP - CH_4	44296	102.73 ± 0.48	Modern	-77.2
Apr - SRb - CH_4	40492*	102.40 ± 0.51	Modern	-86.6
Apr - SRc - CH_4	40505*	104.56 ± 0.53	Modern	-92.1
Apr - DR - CH_4	46329*	99.00 ± 0.94	81 ± 77	-76.0
Sept - SPa- CH_4	43509	105.46 ± 0.49	Modern	-76.9
Sept - SPb- CH_4	46330*	104.78 ± 1.01	Modern	-73.0
Sept - SPc- CH_4	43510	105.26 ± 0.47	Modern	-71.8
Sept - DP- CH_4	43511	103.16 ± 0.48	Modern	-75.1
Sept - SRa- CH_4	43514	103.04 ± 0.48	Modern	-60.5
Sept - SRb- CH_4	46331*	103.71 ± 1.44	Modern	-70.7
Sept - SRc- CH_4	43515	104.89 ± 0.46	Modern	-60.7
Sept - DR- CH_4	43516	102.07 ± 0.48	Modern	-65.9
Chamber CO_2				
Apr - Peatland- CO_2	43494	104.79 ± 0.49	Modern	-25.9
Apr - Riparian -CO_2	43496	100.55 ± 0.47	Modern	-26.6
Apr - Evasion - CO_2	43490	98.86 ± 0.46	36 ± 37	-17.4
Sept - Peatland- CO_2	43500	105.70 ± 0.49	Modern	-26.3
Sept - Riparian -CO_2	43504	100.99 ± 0.47	Modern	-27.1

Sept - Evasion - CO_2	43498	101.39 ± 0.45	Modern	-20.5
Chamber CH_4				
Apr - Peatland- CH_4	43491	107.29 ± 0.48	Modern	-63.2
Apr - Riparian - CH_4	43495	101.79 ± 0.48	Modern	-75.9
Apr - Evasion - CH_4	43489	93.19 ± 0.44	537 ± 38	-58.1
Sept - Peatland- CH_4	43499	108.25 ± 0.50	Modern	-58.0
Sept - Riparian - CH_4	43501	104.84 ± 0.49	Modern	-63.5
Sept - Evasion - CH_4	43497	95.96 ± 0.45	310 ± 38	-54.3
DOC				
Apr - SP - DOC	44314	104.94 ± 0.49	Modern	-27.5
Apr - DP - DOC	44315	104.79 ± 0.49	Modern	-28.1
Apr - SR - DOC	44316	105.14 ± 0.49	Modern	-28.1
Apr - DR - DOC	44317	104.87 ± 0.46	Modern	-28.2
Apr - Stream - DOC	44318	100.41 ± 0.47	Modern	-28.7
Sept - SP - DOC	44319	102.16 ± 0.47	Modern	-27.6
Sept - DP - DOC	44320	100.42 ± 0.47	Modern	-27.7
Sept - SR - DOC	44321	96.01 ± 0.45	327 ± 37	-27.7
Sept - DR - DOC	44324	98.55 ± 0.46	117 ± 37	-27.9
Sept - Stream - DOC	44325	106.47 ± 0.49	Modern	-28.7

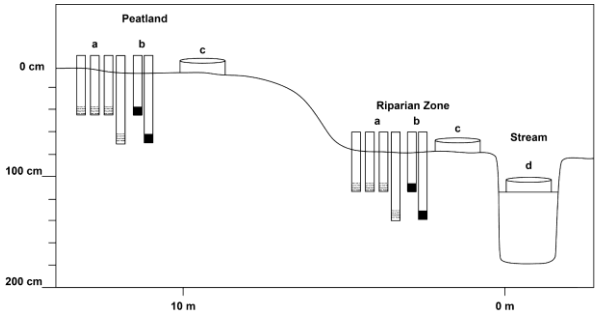


Fig. 1 Schematic of the transect setup used in this study. Sampling probes installed at 40 cm and 70 cm depth for the collection of (a) soil gases (CO_2 and CH_4) and (b) soil DOC in both the peatland and riparian zone. Chambers (c) and (d) represent static chambers for the collection of soil emission CO_2 and CH_4, and a floating chamber for the collection of evasion CO_2 and CH_4, respectively

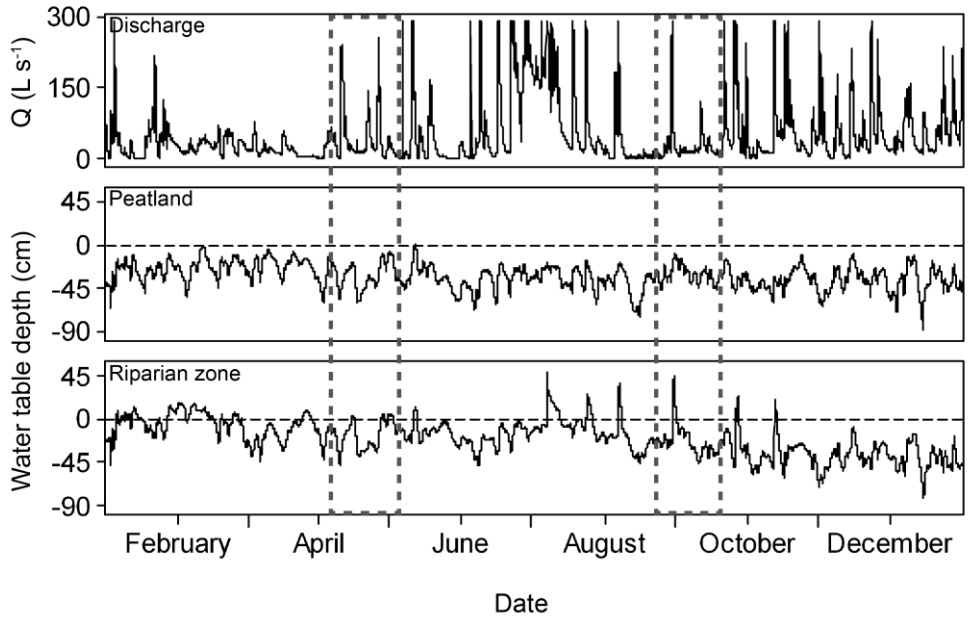
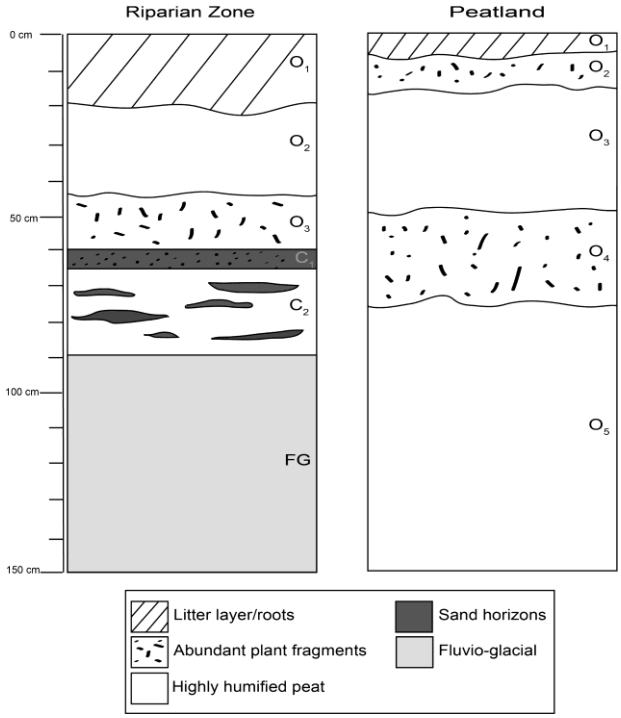
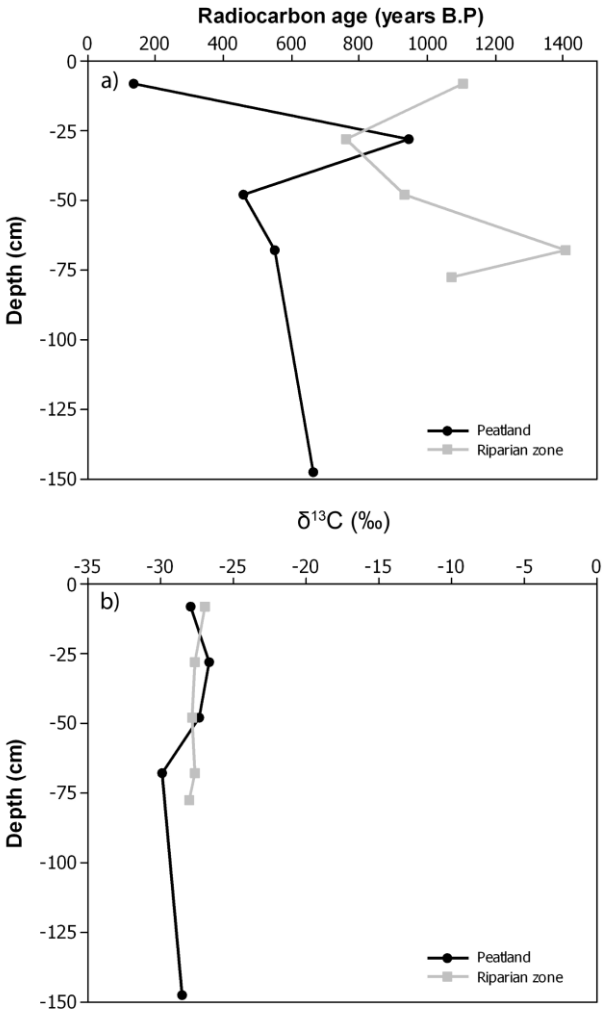


Fig. 2 Graphs showing a) Discharge (Q), b) water table position in the peatland and c) water table position in the riparian zone across the full year 2012. The April and September isotope sampling periods are highlighted by dashed boxes



1019

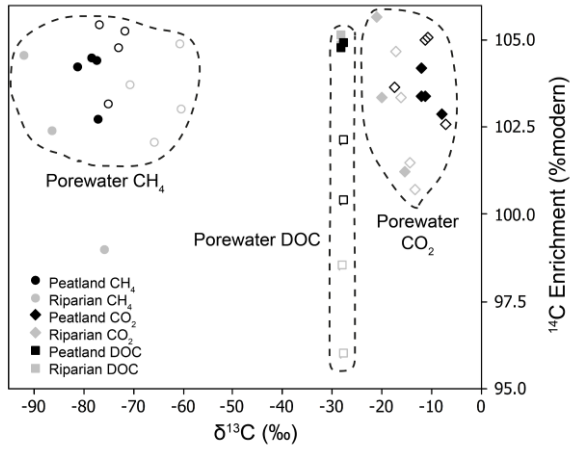
1020 **Fig. 3** Soil profiles from 0 to 150 cm for the riparian zone and the peatland. O1, O2, O3, O4 and O5 represent
1021 organic soil horizons, C1 and C2 represent organo-mineral horizons and FG represents the underlying fluvio-
1022 glacial horizon



1023

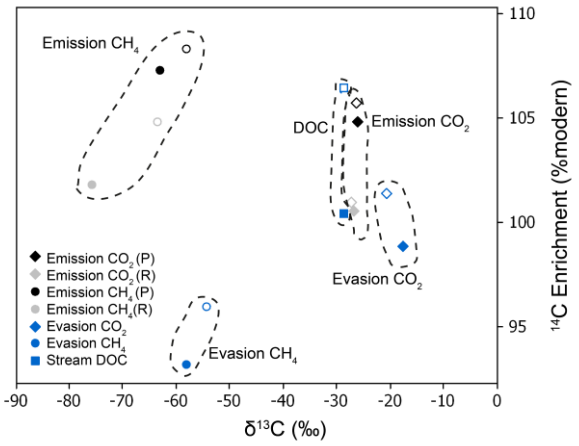
1024 **Fig. 4** Soil profiles of a) radiocarbon age (years BP) and b) $\delta^{13}C$ (‰) in the peatland and riparian zone

1025



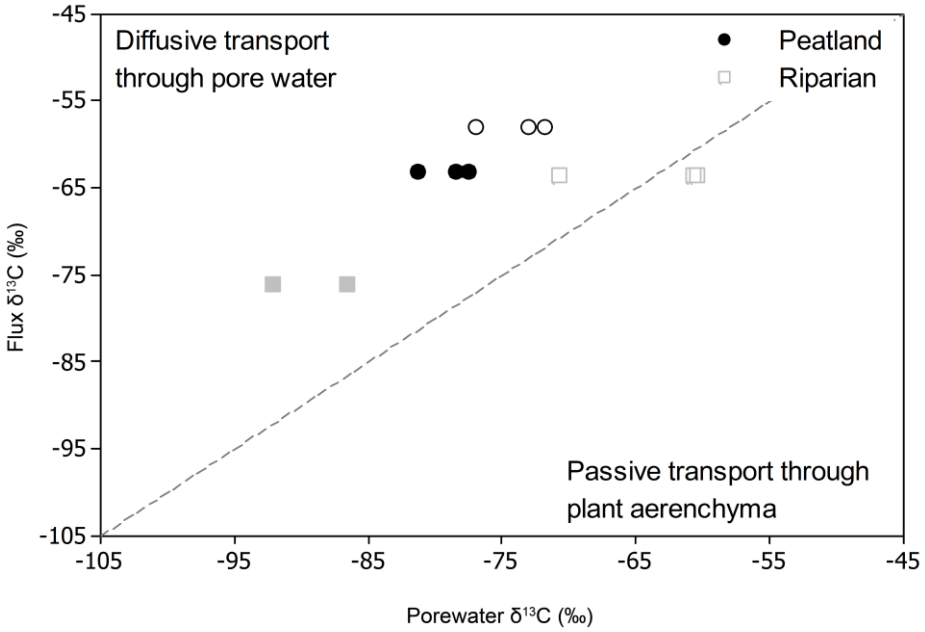
1026

1027 **Fig. 5** ^{14}C / $\delta^{13}C$ scatterplot of porewater CO_2, CH_4 and DOC. Closed symbols represent the April sampling
1028 period and open symbols September. The dashed boxes highlight the clustering of the carbon species



1029

1030 **Fig. 6** ^{14}C / $\delta^{13}C$ scatterplot of emissions from the soil surface of the peatland (P) and riparian (R), stream
1031 evasion and lost downstream as DOC. Closed symbols represent the April sampling period and open symbols
1032 September. The dashed boxes highlight the clustering of the carbon species



1033

1034 **Fig. 7** Flux pathway adapted from Hornibrook (2009). Closed symbols indicate the April period and open
1035 symbols September. The dashed 1:1 line represents transport without partitioning such as via ebullition events